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金属原子线和分子结的 STM 裂结技术构建及其量子输运研究

Construction of Metal Atomic-size Wires and Molecular Junctions and their Quantum Transport Investigation by STM-BJ Techniques

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Construction of Metal Atomic-size Wires and Molecular Junctions and Their Quantum Transport Investigations by STM-BJ Techniques

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目 录

Table of Contents

摘 要

金属原子线和金属-分子-金属结（分子结）表现出特殊的量子输运性质，是纳电子学和分子电子学的重要研究内容。单分子结电导受到自身结构、金属与分子之间的接触构型和能级耦合及周围环境等因素的影响，其机理仍需进一步探讨，其中金属原子线和分子结的构建和电导测量是关键问题。STM 裂结法（STM-BJ）是构建分子结的成功方法之一。然而，迄今为止的所有 STM-BJ 实验，无论是真空中、大气下，还是电化学中，都从相同金属材料的针尖和基底开始，导致缺乏普适性，如对一些软质金属或难以依靠机械撞击形成原子线的过渡金属的研究较为困难，由此也限制了以这些金属作为电极的分子结构建及其电导的系统研究，迫切需要寻找新的技术来获得突破。

本论文针对纳电子学和分子电子学的研究现状和问题，在建立STM-BJ测量平台的基础上，进一步探索单分子结电导及其影响因素；同时，发展STM-BJ技术，建立构建金属原子线及其电导测量的新方法，使STM-BJ技术更具普适性，并能应用于构建非金电极的金属-分子-金属结及其电导测量。主要研究内容和结论如下：

1、搭建了 STM-BJ 电导测量平台。以 Au 为电极，研究了 4,4′-联吡啶（BPY）及其中间插入共轭 CH=CH 键（BPY-EE）和非共轭 CH_2-CH_2 键（BPY-EA）的衍生物单分子结的电导。研究结果表明，这类分子都存在高、低两套电导值，每套电导大小的顺序皆为：BPY > BPY-EE > BPY-EA，且高值电导是低值电导的 8-10 倍，高、低电导由分子的锚定基团与金属电极的接触构型不同引起的。BPY-EA 和 BPY-EE 电导的差异，揭示了在两个吡啶环中间插入 CH_2-CH_2 和 CH_2=CH_2 对分子内电子耦合的影响。

2、提出和建立了基于 jump-to-contact 机制的电化学 STM-BJ 方法，用于测量金属原子线电导。运用电化学 STM-BJ 方法，结合离子液体, 成功测量了 Cu、Pd 和 Fe 三种不同性质的金属原子线电导，演示了该方法的可行性和普适性, 在构建过渡金属原子线及其电导测量方面具有优势。所测的 Cu，Pd 和 Fe 的原子线电导分别为 1 G_0、0.9 G_0 和 0.86 G_0。

3、运用电化学 STM-BJ 方法现场构建了 Cd-Au 和 Zn-Au 合金原子线并测量

其电导。研究发现，调节基底和针尖电位可以改变 Cd-Au 合金的原子线电导；在进一步改进电化学 STM-BJ 方法的基础上，尝试了构建不同金属电极材料的分子结，初步研究了 Cu-HOOC$(CH_2)_2$COOH-Cu 的电导，发现与 Au-HOOC$(CH_2)_2$COOH-Au 电导存在明显差异。

4、作为另一部分独立工作，利用 STM、循环伏安法和 XPS 等方法，研究了金属-有机配合物的自组装，观察到 RhCl(CO)$(PPh_3)_2$ 在 Au(111)的有序结构和电催化析氢作用，提供了获得单分散电催化活性中心的方法，在催化剂的重复利用及基于分子的催化机理的理解具有重要意义。

关键词：量子输运；电化学；分子结；金属原子线；扫描隧道显微镜裂结法；电导测量

Abstract

Metal atomic-size wires and metal-molecule-metal junctions exhibit novel quantum transport properties, which are one of the focuses in nano-electronics and molecular electronics. The conductance of the single molecular junction depends not only on the intrinsic properties of the molecule, but also on the surrounding environment, contact geometries and energy-level alignment of the molecule-electrode contact. Understanding of the conduction mechanism of single molecular junctions and various influences are far from completeness. Further investigation relies on the construction and conductance measurement of the molecular junctions as well as the metal atomic-size wires. Scanning tunneling microscope-break junction (STM-BJ) is one of the most successful methods in the construction of metal atomic-size wires and metal-molecule-metal junctions. However, the conventional STM-BJ technique is based on mechanical crashing of two electrodes with same material, which limits its capability to create chemically well-defined atomic-size wires of transition metals and soft metals, no matter in vacuum, ambient and electrochemical environments. Correspondingly, this restricts construction of metal-molecule-metal junctions with those metals and thus hinders systematic studies of the metal-molecule-metal junctions. Therefore, there is an urgent need to develop new techniques in order to make a breakthrough.

In view of the current research status and the problems encountered in the nano-electronics and molecular electronics, this thesis focuses mainly on the set up and then development of the STM-BJ test bed, which enables the construction of various kind of metal atomic-size wires and single molecular junctions involving those metals as well as systematic studies of electron transport of single molecular junctions and various influences. The main research contents and conclusions are listed as follows:

1. The STM-BJ test-bed for conductance measurement has been set up. The single molecule junction conductance of dipyridines (BPY) with conjugated ethene

(BPY-EE) and nonconjugated ethane (BPY-EA) groups have been measured. All three molecules have two sets of conductance values and both show the order of BPY > BPY-EE > BPY-EA. The high conductance values are about 8-10 times higher than the low conductance values, which are caused by the different contact geometries of metal and molecular anchoring group. The decrease in conductance of BPY-EA with respect to that of BPY-EE reveals the degree of electron decoupling upon insertion of ethene and ethane between the two pyridyl rings.

2. An electrochemical STM-BJ technique has been established for conductance measurement of metal atomic-size wires through a jump-to-contact mechanism. Together with the employment of room temperature ionic liquids, the reliability and generality of this strategy has been proven by the successful conductance measurements of three different types of metals of Cu, Pd and Fe, among them the conductance of Pd and Fe has been found otherwise difficult to measure at room temperature. The preferential quantum conductance at ~1, 0.9, and 0.86 G_0 was measured for Cu, Pd, and Fe, respectively.

3. Employing the electrochemical STM-BJ, alloy atomic-size wires of Cd-Au and Zn-Au are created and their conductance measured. By tuning the potentials of the substrate and tip, the conductance of the Cd-Au alloy atomic-size wires can be changed. Construction of metal-molecule-metal junctions with several metals are attempted by using the electrochemical STM-BJ. Cu-HOOC$(CH_2)_2$COOH-Cu junctions are successfully constructed, whose conductance shows a noticeable difference from the that of the Au-HOOC$(CH_2)_2$COOH-Au junctions.

4. As an independent part of the thesis work, self-assembly of a metal-organic complex molecule, *trans*-RhCl(CO)$(PPh_3)_2$, on Au(111) surfaces and its electrocatalytic properties toward the hydrogen evolution reaction (HER) are investigated by employing scanning tunneling microscopy (STM), cyclic voltammetry (CV), and X-ray photoelectron spectroscopy (XPS). The work provides a mean to quantitatively introduce molecular-dispersed electrocatalytic active sites, which is highly desirable in view of reusability of the catalysts as well as clear understanding of the mechanism of the molecular-based catalysis.

Key words: Quantum transport, electrochemistry, molecular junctions, atomic-size wires, Scanning tunneling microscope-break junction (STM-BJ), conductance measurement